

Laid Open Patent Journal, Sho 61-28441, February 8, 1986

54: Title of invention - A method of manufacturing a pH sensitive microcapsule

21: Patent Application - Sho 59-149689

22: Date of application - July 20, 1984

72: Inventors - Mitsuo Okabe

Hanamigawa Lion's Plaza 4-205, 1508 Chosakumachi

Chiba-shi

Masahiro Takizawa

4786 Ohaza Todoke-su Kawasatomura Kitasaitama-gun

Saitama-ken

Hideyuki Takahashi

4-17-10-501 Isobe Chiba-shi

71: Applicant - Lion K.K.

1-3-7 Honjo Sumida-ku Tokyo-to

Specification

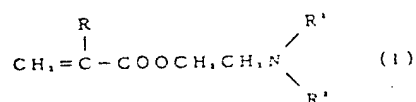
1. Title of invention

A method of manufacturing a pH sensitive microcapsule

2. Claims:

(1) A method of manufacturing a pH sensitive microcapsule in which a core material is dispersed into a dispersion solvent dissolving copolymers containing

(A) at least one kind of basic monomer having the general formula (I),



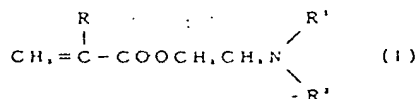
(In the formula, R is hydrogen or methyl group. R1 and R2 are alkyl group of C1 - C3),

(B) at least one kind of water insoluble or hardly water soluble monomer, and

(C) at least one kind of water soluble monomer, and a liquid hydrocarbon is added to the said dispersion solution.

(2) A method of manufacturing a pH sensitive microcapsule in which a core material is dispersed into a dispersion solvent dissolving copolymer containing

(A) at least one kind of basic monomer having the general formula (I),



(In the formula, R is hydrogen or methyl group. R1 and R2 are alkyl group of C1 - C3, respectively.),
(B) at least one kind of water insoluble or hardly water soluble monomer, and
(C) at least one kind of water soluble monomer,
and after the said dispersion solution is dispersed into an oil system, a liquid hydrocarbon is added to the said dispersion system.

3. Detailed explanation of the invention.

Industrial application

The present invention refers to a method of manufacturing a pH sensitive microcapsule. In other words, the present invention relates to a method of manufacturing a microcapsule which is substantially insoluble in the alkaline solution and is soluble in the neutral solution; in other words, the microcapsule exhibits a selective solubility according to the pH of the system. The said microcapsule can be used effectively as the auxiliary agent for laundering along with an alkaline detergent.

The conventional technology

In case of manufacturing a microcapsule containing active ingredient as the core material, whereas the material used for coating the core material is pH sensitive, the core material can be released conveniently according to the pH condition of the solution system.

One of typical application of such microcapsule is an auxiliary agent for laundering combined with alkaline detergent composition.

In general, the laundering process using a washer consists of water supply, washing, spinning (dehydrating), rinsing and spinning (dehydrating). In order to use effectively the auxiliary agent composition for laundering such as fabric softener, finishing agent, etc., these agents have been added after completing the washing process. In the past, a housewife operated these laundering steps manually. In this case, the addition of a softener, bleaching agent, starching agent, and other auxiliary agents after completing the rinsing step was not so difficult. However, since the use of semi-automatic or fully automatic washer has become very popular in recent years, the addition of such auxiliary agents has not yet been operated automatically although the laundering processes have been automated completely.

Problems to be solved in the present invention

In case of coating the auxiliary agent for laundering with polymer which is substantially insoluble in alkaline detergent solution and is soluble in neutral rinsing solution, the active ingredient in the auxiliary agent is protected from the alkaline washing solution during washing stage and can be released into the rinsing solution during the rinsing stage. In this case, the effect of the auxiliary agent can be used efficiently and furthermore, the process of adding the auxiliary agent during the laundering process can be eliminated since the auxiliary agent is added at the beginning of the laundering process.

There are several different kinds of polymers which can show different

solubility in the different pH ranges. For example, although polyvinyl-acetal diethylaminoacetate is insoluble in water at neutral range, the said compound is soluble when the pH of the system is lower than 5.8. On the other hand, although the copolymer of vinylpyrrolidine and acrylic acid is soluble in water when the pH is lower than 4 or is higher than 7.4, the compound is insoluble in water when the pH range is between 4 and 7.4. However, there have been no informations on the polymer which are insoluble in alkaline water, but is soluble in neutral and acidic water; in addition, the solubility of which can alter within a narrow range of pH. The present inventors have proposed the said copolymers and auxiliary agents coated with the said copolymers in Patent Journal Sho 58-247997.

However, in case of coating the core material such as the auxiliary agent for laundering, etc. with the copolymer, it is necessary for the core material to be coated perfectly with the coating agent in order to have the effective release of the core material in the system. On the other hand, it is frequently requested to have smaller coated particles. For example, as the auxiliary agent for laundering is adsorbed on the cloth and remains on the cloth after washing and is subjected for spinning and rinsing processes, it is preferable for the agent to be small in the size in order to have an efficient adsorption onto the textile and to avoid any ill-feeling of the agent during wearing. Furthermore, it is also necessary to regulate a proper granular size of the product in order to prevent the aggregation and the segregation in the composition.

Composition of the invention

The purpose of the present invention is to provide a method of manufacturing a microcapsule which can hold completely the core material in the alkaline solution and release the core material into the neutral or acidic solution.

The purpose of the present invention is to provide a method of manufacturing effectively microcapsules having a small diameter.

Furthermore, the purpose of the present invention is to provide a method of manufacturing microcapsule, whereas the size of the microcapsule is easily regulated.

In other words, the first claim of the present invention is a method of manufacturing a pH sensitive microcapsule manufacturing process consisting of the following processes (a) and (b).

- (a) A process of dispersing a core material into a dispersion solvent containing a copolymer containing the following 3 monomers (A), (B) and (C).
- (A) at least one kind of basic monomer having the general formula (I),



- (In the formula, R is hydrogen or methyl group. R1 and R2 are alkyl group of C1 - C3),
- (B) at least one kind of water insoluble or hardly water soluble monomer, and
 - (C) at least one kind of water soluble monomer,
 - (b) A process of adding a liquid hydrocarbon to the dispersion solution obtained at the process (a).

The second claim of the present invention introduces the following the process (a') between the said processes (a) and (b), and the dispersion solution obtained at the process (a') is treated in the process (b).

- (a'). A process of dispersing the dispersion solution obtained at the process (a) into an oil system.

The basic monomer (A) having the general formula (I) is the major monomer ingredient for manufacturing the pH sensitive copolymer employed in the present invention. For example, these monomers are acrylic acid N,N-dimethylaminoethyl, methacrylic acid N,N-dimethylamino ethyl, acrylic acid N,N-diethylaminoethyl and methacrylic acid N,N-diethylaminoethyl, and so on. These compounds can be used singly or as a combination of more than two kinds.

Water insoluble or hardly water soluble monomer of the ingredient (B) is the agent contributing the expansion of the water insoluble pH range of the pH sensitive copolymer.

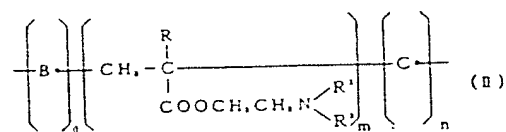
Practical examples of the said compounds are acrylic acid ester, methacrylic acid ester, crotonic acid ester, itaconic acid ester, vinylacetate and styrene. One or more than two kinds of the said compounds can be used in the present invention. In case of using alkyl ester of acrylic acid, methacrylic acid, crotonic acid and itaconic acid as the monomer (B), the compound having alkyl group C1 - C18 (ester bond) can be used. However, when the alkyl chain length is too long, the rate of solubility of the copolymer in alkaline water becomes slow. Consequently, the chain length of the alkyl group may be 1 - 8. Preferable examples are acrylic acid ethyl, acrylic acid methyl, acrylic acid butyl, methacrylic acid methyl and methacrylic acid ethyl.

Water soluble monomer (C) is an ingredient capable of contributing the expansion of the soluble pH range of the pH sensitive copolymer.

The practical examples of the said water soluble monomer (C) in the invention are N,N-dimethylaminopropyl acrylic acid (or methacrylic acid) amide, N,N-dimethylaminomethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminoethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminobutylacrylic acid (or methacrylic acid) amide, 2-hydroxyethylacrylic acid (or methacrylic acid), 2-hydroxypropylacrylic acid (or methacrylic acid), polyethyleneglycol or methoxypolyethyleneglycol, (In both cases, an average adduct of ethylene glycol : $p = 2 - 30$), ester of acrylic acid or methacrylic acid. These compounds can be used singly or as a combination of more than two kinds.

The copolymer ratio of these monomers can be selected properly according to the setting of soluble pH range and insoluble pH range in relation

to the purpose of use of the microcapsule. In case of using a microcapsule as the auxiliary agent for laundering, it is preferable that the capsule is insoluble in alkaline solution (higher than pH 9.5) and is soluble in weak alkaline to acidic solution (lower than pH 8.5) and at the same time the solubility ratio under the presence of surfactants is large. In order to obtain such microcapsules, it is preferable that $l / (l + m + n) = 0.08 - 0.45$ and $m / (l + m + n) = 0.1 - 0.65$ in the general formula (II), preferably $l / (l + m + n) = 0.1 - 0.4$ and $m / (l + m + n) = 0.15 - 0.55$.



(In the formula, B. and C. are the constituent units of monomer (B) and the monomer (C), respectively.).

The degree of polymerization ($l + m + n$) may be 100 - 50,000, preferably 300 - 20,000.

The copolymers described in the present invention can be manufactured by the conventional radical polymerization reaction under normal pressure or positive pressure. The solvents used in the said polymerization may be acetone, benzene, toluene, chloroform, ethylacetate, isopropanol, dimethylformamide, dimethylsulfoxide, etc. or a mixture of these solvents or solvent systems containing water. The radical polymerization initiator may be azo-bis-isobutyronitrile, triphenylmethylazobenzene, etc. The concentration of the initiator per the total amount of monomers may be 2 - 100 mmol.

The polymerization temperature and the time may be different according to the type of polymerization solvent systems and combinations of various monomers. However, it is usually 40 - 90° C and 5 - 20 hours, respectively. The concentration of monomers in the reaction system can be determined properly according to types of solvents, polymerization temperature and type of initiator for the polymerization. However, it is usually 20 - 80 weight %.

The method of manufacturing microcapsules described in the present invention is based on the coacervation method using the said pH sensitive copolymer. The said copolymer is dissolved in the dispersion solvent for the core material. The core material is dispersed into the said solvent system by means of stirring, or mixing. The dispersion solvent can dissolve copolymer and disperse core materials. The practical examples of the said solvents are the said solvents used for polymerization and alcohols. Among these solvents, acetone is preferable. The concentration of the copolymer in the dispersion solvent may be 1 - 70 wt%. In case of employing the manufacturing process consisting of no (a') process in which the dispersion solution is mixed with an oil ingredient, the concentration may be 1 - 30 wt %. On the other hand, in case of employing the manufacturing process consisting of the said

(a') process, it may be 10 - 70 wt%. Furthermore, the amount of core material dispersed in the solvent per the unit amount of polymer may be 0.2 - 10 times (as much as the amount of polymer).

The core material can be selected properly according to the purpose of use of the capsule. One of the typical application of the microcapsule may be the auxiliary agent for laundering.

The auxiliary agents for laundering may be long chain dialkyldimethyl ammonium salt, 1-methyl-1-long chain alkanoylaminoethyl-2-long chain alkyl imidazolium salt, long chain dialkyl dimethyl ammonium salt, mixture of fatty acid salts (fabric softeners), suds depressants such as silicone oil, etc., bleaching agents such as hypochlorite, percarbonate, organic peroxides, etc., starching agents, blue coloring agent, fluorescent whitening agent, enzyme, etc.

A liquid carbon is added to the dispersion solution where the core material has been dispersed. The said addition step can be carried out at 20 - 40° C. Liquid hydrocarbons are aliphatic hydrocarbons of C5 - C12 such as n-hexane, n-heptane, n-octane, etc., petroleum ether, petroleum benzene, etc.

When the concentration of the liquid hydrocarbon exceeds a certain level, the phase separation occurs and the microcapsule is formed. After adding the liquid hydrocarbon, the system is allowed to cool at 5 - 10° C and the particles are recovered by proper separation methods such as centrifugation, filtration, etc. After washing with liquid hydrocarbon, microcapsules can be obtained. The concentration of liquid hydrocarbon per the dispersion solvent may be 40 - 100 weight %.

On the other hand, the dispersion solvent for the core material and the oil ingredient can be mixed prior to the addition of the core material in the said solvent system, and the dispersion solution containing the oil ingredient can be prepared. In this case, it is preferable that 10 - 100 weight parts of the dispersion solution containing copolymer per 100 weight parts of the oil ingredient can be used (Preferable amount may be 10 - 50 weight parts).

The oil ingredients are an oil material which is liquid at room temperature and are liquid paraffin, vegetable oils, etc. The preferable oil ingredients in the present invention may be liquid paraffin. Although the liquid paraffin is oil consisting of purified saturated hydrocarbons and various grades of the said preparation are available. The preferable preparation is 100 cst (37.8° C) in the viscosity or less.

When the liquid hydrocarbon is added, the phase separation occurs, and a thick polymer coats the core material. After adding an excess amount of liquid hydrocarbons, the microcapsules can be recovered in the same manner as described before. The amount of liquid hydrocarbon may be 70 - 150 % of the oil ingredients (volume).

It is not essential that the liquid hydrocarbon and the oil ingredients are solubilized. In other words, these ingredients may be separated. However, a combination of the said liquid hydrocarbon and the oil ingredients showing the relative solubility may be selected.

In order to prevent the aggregation of microparticles, before separating the microcapsule particles, micropowder such as silica, titanium oxide, diatom earth, cellulose, etc. can be added.

Function

The present invention is a method of manufacturing microcapsules by utilizing the coacervation method. The core material is dispersed into the dispersion solvent containing copolymer and a defined amount of liquid hydrocarbon is added to the said dispersion solution. In this case, a phase separation occurs and the separated phase coats the core material. Thus, a microcapsule showing the pH sensitivity can be obtained. This microcapsule resembles the primary granule of core material dispersed by stirring.

When the phase separation is induced under the presence of the oil ingredient by adding oil ingredient prior to the addition of liquid hydrocarbon, the diameter of the microcapsule can be regulated by controlling the concentration of the oil ingredients and the stirring condition.

Effectiveness

According to the method of manufacturing described in the present invention, microcapsules having a small diameter which are thoroughly coated with the coating substance, are insoluble in the alkaline solution and are soluble in neutral to acidic solution so that the core material can be released into the neutral to acidic solution, can be manufactured.

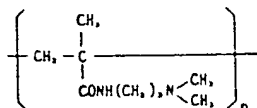
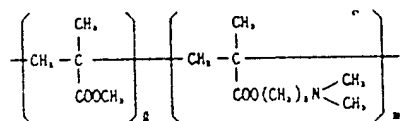
On the other hand, in case of inducing the microcapsulation under the presence of oil ingredients, the diameter of the microcapsule can be regulated.

When the said microcapsule is used for preparing the auxiliary agent for laundering, whereas the said agent is used as the core material of the microcapsule, it is very effective to prepare the additive agent for the alkaline detergent used in the fabric laundering.

Practical examples:

Practical example 1.

Twenty g of powder distearyl dimethyl ammonium chloride (passed a 100 mesh sieve) was dispersed into 120 g of acetone solution containing 15 weight % of water soluble polymer containing tertiary amine having the following chemical structure by stirring, and while stirring, 90 g of n-hexane was added dropwisely at 25° C.

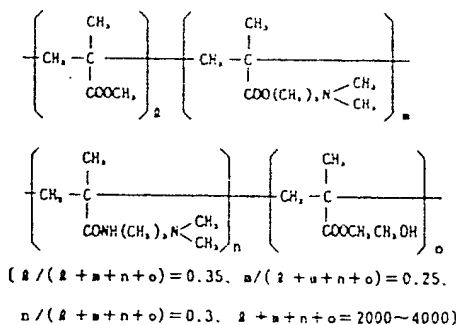


$$\begin{aligned} (l / (l + m + n)) &= 0.4, \quad m / (l + m + n) = 0.15, \\ l + m + n &= 1000 \sim 1500 \end{aligned}$$

After cooling down to 5° C, 2 g of micropowder silica was added. After stirring, the mixture was filtered through a filter paper. The residue was washed with n-hexane and was dried. The microscopic examination of the product demonstrated microcapsules of 30 - 200 microns in the diameter, whereas micropowder of distearyl dimethyl ammonium chloride was coated 100 % with water soluble polymer showing the said chemical structure. The said capsule could be used as the auxiliary agent for laundering which could provide the softness on the textiles.

Practical example 2:

Twenty g of micropowder distearyl methyl ammonium chloride was dispersed into 70 g of acetone solution containing 20 weight % of water soluble polymer containing tertiary amine group having the following chemical structure, and the mixture was then dispersed into 150 g of liquid paraffin (viscosity : 14 cst., at 37.8° C). After adding 150 ml of n-hexane, the mixture was allowed to cool to 5° C, and then was filtered through a filter paper. The residue was washed with n-hexane and was dried. In this case, microcapsules of 100 - 300 microns in the diameter containing micro powder of distearyl dimethyl ammonium chloride coated 100 % with polymer containing tertiary amine group having the following chemical structure were obtained. These capsules could be used as the auxiliary agent for laundering which could provide the softness on the textile.



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.